THE JOHN DUNCAN FUND

MR. JOLLY informs us that the subscriptions sent to form a fund to raise this old botanist above the need of parochial relief and provide for his comfort during his remaining years, has already reached a considerable sum, all which has been sent spontaneously from all parts of the country, without the formation of any committee or pressure whatever. More is coming in daily, and the old man's future independence would seem in the end to be pretty well assured. The sympathy shown in the case has been widespread and of the warmest kind. Her Majesty the Queen has graciously sent 10*l.*, and the Duke of Argyll, who sent 10*l.* at first, writes that it is a subscription which ought to be zealously supported by all who are interested in the pursuit of science, and who honour the high moral and intellectual qualities by which John Duncan is distinguished. All this speaks well for the generosity of the country, but more is required. The case is without doubt unusually deserving.

The following is a list of the subscriptions which have been received at this office during the past week:—

	£	s.	d.
Amount previously announced	11	15	0
Matthew Gray ...	2	0	0
F. A. Hamilton ...	2	0	0
Received in Registered Letter ...	2	0	0
Jas. Greig	0	10	0
George Russell ...	0	10	0
Thomas Clarke ...	1	1	0
A Friend	0	10	0
L. M.	3	3	0
E. V.	0	2	6
Miss Wilson	0	5	0
Isaholt Fraser ...	0	3	0
Mrs. Tuckwell ...	0	10	0
Alfred Shipley ...	1	1	0
E. H. Millar	1	0	0
John Noble	5	0	0
W.	0	10	0
Clay, Sons, & Taylor	1	1	0
Dr. Sim	1	0	0
Henry Stretch	0	2	0
A. A. Rathbone ...	3	0	0
A. G.	0	10	0
Sidney Billing	0	10	0
A. W. Agnew	1	0	0
Orry's Dale	0	5	0
John Renton Dunlop.	1	0	0
Prof. Prestwich, F.R.S.	2	2	0
George Knott	1	1	0
H. F. R.	0	10	0
Mrs. Henry	1	0	0
Miss Weir	0	10	0
An Old Woman ...	0	2	6
A. E.	0	10	0
J. B. B.	2	2	0
	48	6	0

EXPERIMENTS ON ICE UNDER LOW PRESSURES

CERTAIN theoretical considerations on the relations of the solid, liquid, and gaseous states of matter led me three or four years ago to the speculation that in a perfect vacuum the liquid state would be impossible, and that under this condition it might be possible to raise bodies to temperatures above their ordinary melting-points. These ideas were mentioned to one or two friends at the time, but they naturally considered them as speculations which would not be verified by experiment. From the pressure of other work the subject was for the time dropped, and it was not till the autumn of 1879 that an experimental investigation was commenced. The first substance tried was sulphur, but this was ultimately found to be unsuitable, as under low pressures, though it apparently boiled as low as 130° C., yet at that or a little above that temperature it began to froth. Naphthalene was then tried, but as the pressure at which the boiling-point fell below the melting-point was less than about 7 mm., it was not easy to *maintain* the pressure at a sufficiently low point. Mercuric chloride however, which was the next body tried, yielded better results.

Mercuric chloride melts at 288°, resolidifies at 270°-275°, and boils at 303°. About 40 grammes of the pure compound were placed in the tube A (Fig. 1), and a thermometer arranged with its bulb imbedded in the salt. The drawn-out end of the tube was connected by stout india-rubber tubing with one branch of the three-wayed tube B, whilst the other was attached to the manometer C. B was connected with a Sprengel pump fitted with an arrangement for regulating the pressure. When the pressure had been reduced by means of the pump to below 420 mm., the mercuric chloride was strongly heated by the flame of a Bunsen's burner, with the following results:—Not the slightest fusion occurred, but the salt rapidly sublimed into the cooler parts of the tube, whilst the unvolatilised portion of the salt shrank away from the side of the tube, and clung tenaciously in the form of a solid mass to the bulb of the thermometer, which rose considerably above 300° C., the mercury shooting up to the top of the stem. After slight cooling, the air was let in, and under the increased pressure thus produced the salt attached to the bulb of the thermometer at once melted and began to boil, cracking the tube at the same time.

The experiment was next varied as follows:—About the same quantity of chloride was placed in the tube as before and heated by the full flame of a Bunsen's burner. The lamp was applied during the whole of this experiment, and the size of the flame kept constant throughout. The

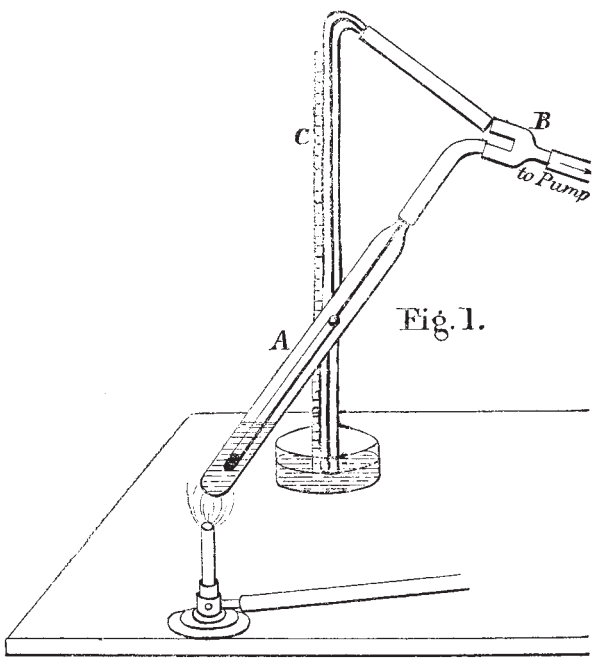

Fig. 1.

mercuric chloride first liquefied and then boiled at 303° under ordinary pressure, and whilst the salt was still boiling the pressure was gradually reduced to 420 mm., when the boiling-point slowly fell to 275°, at which point the mercuric chloride suddenly began to solidify, and at 270° was completely solid, the pressure then being 376 mm. When solidification was complete the pump was stopped working, but the heat still continued to the same extent as before. The salt then rose rapidly to temperatures above that at which a thermometer could be used, but not the least sign of fusion was observed. From the completion of the solidification to the end of the experiment the pressure remained at about 350 mm.

The above experiment, which was repeated three times, shows therefore that when the pressure is gradually reduced from the ordinary pressure of the atmosphere to 420 mm., and the boiling-point simultaneously from 303° to 275°, the salt solidifies while it is still boiling, notwithstanding that it is being strongly heated at the same time, and that, after solidification is complete at 270°, the temperature then rises far above the ordinary boiling-point (303°) of the substance without producing any signs of fusion. Under ordinary circumstances mercuric chloride melts a

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288° and re-solidifies at 270°-275°, *i.e.* at a temperature identical with that at which it solidifies under diminished pressure as above described.

After the above experiments had been made the investigation had to be unavoidably deferred, and was not resumed till last autumn, when a large number of determinations were made of the boiling-points of several different substances under various pressures, and from these was drawn the general conclusion described in a letter to NATURE (vol. xxii. p. 434), in September last, viz.: "In order that any solid substance may become liquid it is necessary that the pressure be *above* a certain point, called the critical pressure, otherwise it cannot be melted, no matter how great the heat applied." Assuming the truth of this conclusion, I set to work to apply it in the case of ice, as it would undoubtedly have the greatest interest in connection with that substance. On this account my experiments since the end of August have related almost solely to ice.

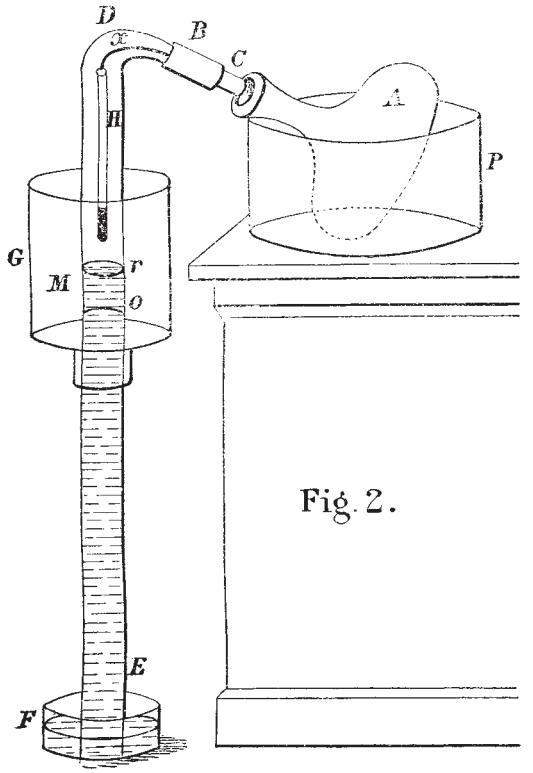

Fig. 2.

The problem to be solved was whether ice could be prevented from melting by maintaining the pressure below its critical pressure, *i.e.* the tension of its vapour at the melting-point, and that whatever the intensity of the heat applied. Now the theory of critical pressure gives us no information as to whether the ice, on non-fusion, would ot would not rise above its ordinary melting-point when strongly boated but as this result had been previously attained in the case of mercuric chloride it appeared not impossible that the ice *might* become hot.

The question as to the rise of temperature of the ice above o°, though at first but a side issue of the investigation, became from its more especial interest the chief object of inquiry, and the experiments which have been made and those which are at present in hand relate almost solely to this point.

The great difficulty to be overcome was to maintain the pressure in the containing vessel below 4·6 mm., *i.e.* the tension of aqueous vapour at the freezing-point; for it will be easily understood that if the ice be but slightly heated the quantity of vapour given off would soon be sufficient to raise the pressure above that point. After several fruitless attempts, the following plan, involving the principle of the cryophorus, was adopted:—A strong glass bottle, such as is used for freezing water by means of Carre's pump, was fitted with a cork and glass tube C (Fig. 2) and the cork well fastened down by copper wire. A and C were then filled with wet mercury (the water facilitating the removal of the air-bubbles) and C connected with the end of the tube D E by means of the stout india-rubber tubing B, a thermometer having been previously attached by the wire x to the lip of the tube at B. The tube D E was about one inch diameter, and about four feet long from the bend to the end E; after connection with C it was completely filled with mercury and the whole inverted over the mercurial trough F, as shown in the figure, when the mercury fell to O, the ordinary height of the barometer. The mercury was run out of A by tilting up the bottle and inclining the tube D E. By this means a Torricellian vacuum was obtained from A to O. D was next brought to the vertical, and the bottle A placed in the trough P. A tin bottle G without a bottom was

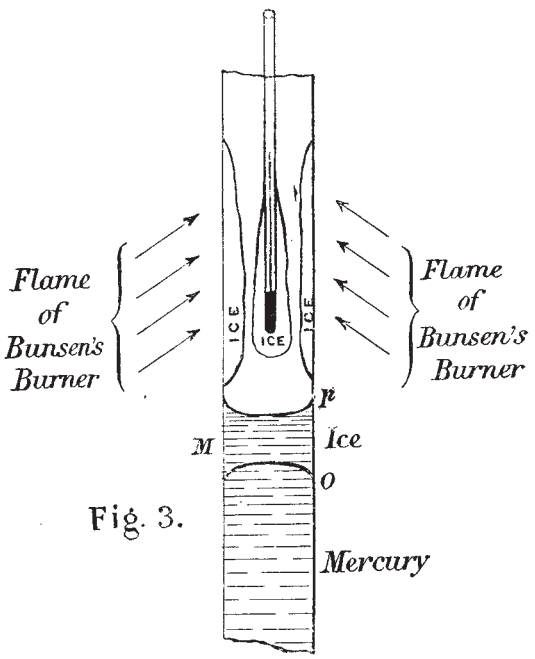

Fig. 3.

fitted with a cork, so that it might slide somewhat stiffly along D E.

To begin with, the tin bottle was placed in the position G and filled with a freezing mixture of salt and ice. Some boiled water was then passed up into the tube D E, sufficient to form a column at M about two inches deep. The thermometer H had been previously arranged so that its bulb might be one or two inches above the surface of the water M. The bottle A was next surrounded by a good quantity of freezing mixture, in order that any vapour given off from the water at M might be condensed in A as fast as it was formed, and thus the internal pressure might never be more than about 1·0 to 1·5 mm. When A had been sufficiently cooled, which required about fifteen minutes, the tin vessel G was slid down the tube D E, and its freezing mixture removed. The water at M had then solidified to a mass of ice, which on heating with the flame of a Bunsen's burner, melted either wholly or partially, and the liquid formed began at once to boil. The fusion commenced first at the bottom of the column of ice, whereas the upper part fused only with difficulty, and required rather a strong heat. The fusion in this case was probably due

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to the steam evolved from the lower portions of the ice column being imprisoned and unable to escape, and hence producing pressure sufficient to cause fusion.

When the greater part of the ice had been melted, the tube was tightly clasped by the hand, the heat of which was sufficient to produce a somewhat violent ebullition. The liquid in boiling splashed up the side of the tube and on to the bulb of the thermometer, where it froze into a solid mass, as represented in Fig. 3. By this means the ice was obtained in moderately thin layers. The tube at the points indicated by the arrows was then strongly heated by the flame of a Bunsen's burner with the following results :—The ice attached to the sides of the tube at first slightly fused, because the steam evolved from the surface of the ice next the glass, being imprisoned between the latter and the overlying strata of ice, could not escape, and hence produced pressure sufficient to cause fusion, but as soon as a vent-hole had been made fusion ceased, and the whole remained in the solid state, and neither the ice on the sides of the tube nor that on the bulb of the thermometer could be melted, no matter how great the heat applied, the ice merely volatilising without previous melting ; thus proving that if the pressure be maintained below the critical pressure the ice cannot be melted. In different experiments the thermometer rose to temperatures considerably above the melting- and even the boiling-point of water, the highest temperature reached being 180° C., when the ice had either wholly volatilised or had become detached from the bulb of the thermometer, but in no case did the ice attached to the thermometer melt when these temperatures had been reached, as erroneously stated in some reports of my experiments. The ice attached to the thermometer did not partially fuse at the commencement of the heating, because, the heat reaching the outer surface of the ice first, evaporation could take place from a free surface and the vapour not become imprisoned, as was the case with the ice attached to the sides of the tube. These experiments were repeated many times with the same result, except in one case in which the heat applied had been very strong indeed, and the ice attached to the sides of the tube fused completely. On removing the lamp however for a few seconds the water froze again, notwithstanding that the portion of the glass in contact with it was so hot that it could not be touched without burning the hand.

The chief conditions necessary for success appear to be (1) that the condenser A (Fig. 2) is sufficiently large to *maintain* a good vacuum. For the size of apparatus given above it ought to be about 1 litre ; (2) that the ice is not in too great mass, but arranged in thin layers. Nor must it expose too great a surface for evaporation, otherwise the steam is liable to be evolved more quickly than it can be condensed, and the pressure would therefore rise above the critical pressure. Further, in the case where the heat is applied to the under surface of the layers of ice, the latter must be sufficiently thin to allow of a vent-hole being formed for the escape of the steam coming from below, if not, fusion occurs. When the heat is applied to the free surface of the ice the layers may be much thicker. In order to get the temperature to rise above the ordinary melting-point of ice, it is necessary that a very strong heat be applied, otherwise all the heat is used to convert the ice into steam without raising its temperature ; it must in fact be applied more quickly than it can be absorbed for changing the state of aggregation. Prof. McLeod, who has written to me to the effect that he has been unable to obtain any symptoms of hot ice, has failed I believe on account of not having complied with this condition. Dr. Lodge, in an admirable and very clear letter to NATURE (vol. xxiii. p. 264), has endeavoured to explain why "hot ice" is possible, and also points out the absolute necessity for supplying the heat more rapidly than it can be absorbed by the vapour.

Now the question arises, Does the thermometer in the above experiments indicate the real temperature of the ice ? It has been said by Prof. Stokes that the ice, though attached to the thermometer, is not at the same temperature as the latter, and that the action is really as follows : The pressure is reduced till the boiling-point falls below the melting-point, and when heat is applied to the ice in contact with the glass tube a film passes into vapour, and thus prevents the ice from touching the glass except at a few isolated points. The great latent heat of evaporation prevents the ice from rising to its ordinary melting-point, and hence no fusion occurs. The ice is only heated —except at the few isolated points of contact—by radiation, and therefore comparatively slowly. A portion of the heat passes through the ice and falls on the thermometer inside, and the latter rises in temperature ; this causes the formation of a film of vapour between the ice and the bulb of the thermometer, so that the latter is in contact with the ice at a few points only, and therefore hardly any heat passes by conduction to the ice.

As under the circumstances of the case this appeared the most probable explanation of the phenomena, it was of great importance to show by other and more conclusive experiments whether the ice really was hot or not. For this purpose Prof. Roscoe suggested the most decisive test which could be applied, viz., dropping the supposed hot ice into water and observing the amount of heating or cooling of the latter. Up to the present I have only had the opportunity of completing two of these calorimetrical determinations, and the second of these was merely a qualitative experiment, as the weight of ice dropped in could not be found, owing to a small quantity of the water having been jerked out of the calorimeter the moment the ice entered it. In both experiments, however, the water distinctly increased in temperature, and therefore showed that the ice must have been above 80° C. In the complete experiment the weight of ice dropped into 185 grammes of water was 1·3 grammes, and the rise in temperature 0·2°C., showing that the temperature of the ice was 122° C. From the nature of the experiment the weight of ice which could be dropped into the calorimeter was only small, and though the rise in temperature was but slight, yet if the ice had been at 0° a relatively large cooling ought to have been observed. Great care was taken to avoid any error in the determinations. The thermometer employed was graduated so as to allow of a difference of 0·05° C. being easily detected, two observers read off the temperatures independently of one another, the calorimeter was inclosed in several casings and filled with the water to be used some hours before the experiment, so that it might have the temperature of the room, whilst the time which elapsed between the readings of the thermometer would not be more than about fifteen seconds, and finally the calorimeter was not brought into position to receive the ice till the source of heat had been removed. To place the point beyond doubt, however, several additional and perfectly satisfactory calorimetrical determinations are necessary, and if possible on a larger scale. Such experiments are at present in hand. In the meantime I would make the following remarks in favour of the high temperature of the ice. If the ice is not really hot, notwithstanding that the thermometer indicates say a temperature of 120° C., how is it possible for the ice to hang on to the thermometer? For if it be separated from the bulb by a layer of steam, it cannot hang by steam, it would at once become detached from the thermometer. The thermometer was chosen so that the bulb was of the same, and in most cases of a less, diameter than the stem, so that there was nothing to prevent the ice falling away if so inclined.

In some cases I have had thin plates of ice attached by their edge at right angles to the stem of a paper scale thermometer for a considerable time without being

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detached or melting, notwithstanding the temperature was so high that the paper scale at that portion of the stem to which the ice clung was charred; this was the case in one of the experiments shown at the Chemical Society. In another instance I have had a thin circular piece of ice attached to the otherwise bare bulb of the thermometer, and though this piece was very thin and no more than about 2 mm. diam., it took fully one minute or more to volatilise, notwithstanding the thermometer indicated a mean temperature of about 70° C., and the surrounding tube was very hot. If the ice were not capable of being heated above its melting-point, a piece so small as that referred to would, I think, under these circumstances have fused or volatilised almost instantaneously. If the ice be really above 80° C. it ought to melt suddenly and at once on discontinuing the heat and increasing the pressure, and this I have in one or two instances found to be the case. Thus in one experiment a beautiful rod of ice nearly six inches long and about half an inch diameter was attached to a glass rod suspended in the apparatus described above and heated very strongly with a large Bunsen's burner for several minutes; the pressure was then let in, when the ice at once fell off the rod into the mercury trough below, melting completely, and as far as could be seen even before it reached the mercury. Careful observations have also been made to see whether any cavity could be detected between the ice and the hot thermometer when the latter was only partially covered with ice, and indicated a high temperature, but such could not be seen either with ice or mercuric chloride. In both cases the substance appeared to rest in actual contact with the bulb of the thermometer, in this respect differing from camphor, which does exhibit such a space. I have however never been able to get camphor above its ordinary melting-point, though by reducing the pressure below 400 mm., it solidifies while boiling, and cannot be re-melted unless the pressure be increased.

One curious point about the ice experiments is the comparative slowness with which the ice appears to evaporate, though the surrounding tube is very strongly heated.

In conclusion, I need hardly say that it is highly desirable that my results should be confirmed by other observers.

THOS. CARNELLEY

TELE-PHOTOGRAPHY

WHILE experimenting with the photophone it occurred to me that the fact that the resistance of crystalline selenium varies with the intensity of the light falling upon it might be applied in the construction of an instrument for the electrical transmission of pictures of natural objects in the manner to be described in this paper.

In order to ascertain whether my ideas could be carried out in practice, I undertook a series of experiments, and these were attended with so much success that although the pictures hitherto actually transmitted are of a very rudimentary character, I think there can be little doubt that if it were worth while to go to further expense and trouble in elaborating the apparatus excellent results might be obtained.

The nature of the process may be gathered from the following account of my first experiment. To the negative (zinc) pole of a battery was connected a flat sheet of brass, and to the positive pole a piece of stout platinum wire; a galvanometer was interposed between the battery and the brass, and a set of resistance-coils between the battery and the platinum-wire (see Fig. 1, where B is the battery, R the resistance, P the wire, M the brass plate, and G the galvanometer). A sheet of paper which had been soaked in a solution of potassium iodide was laid upon the brass, and one end of the platinum wire previously ground to a blunt point was drawn over its surface. The path of the point across the paper was marked by a brown line, due, of course, to the liberation of iodine. When the resistance was made small this line was dark and heavy; when the resistance was great the line was faint and fine; and when the circuit was broken the point made no mark at all. If we drew a series of these brown lines parallel to one another, and very close together, it is evident that by regulating their intensity and introducing gaps in the proper places any design or picture might be

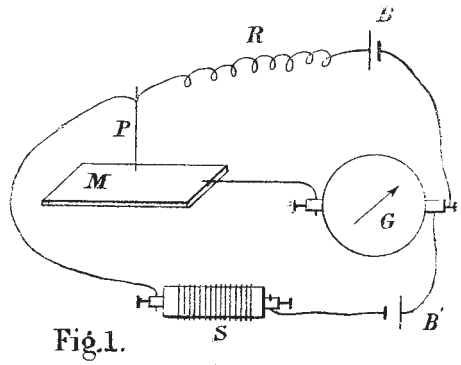

Fig. 1.

represented. This is the system adopted in Bakewell's well-known copying telegraph. To ascertain if the intensity of the lines could be varied by the action of light, I used a second battery and one of my selenium cells, made as described in NATURE, vol. xxiii. p. 58. These were arranged as shown in Fig. 1, the *negative* pole of the second battery, B', being connected through the selenium cell S with the platinum wire P, and the positive pole with the galvanometer G. The platinum point being pressed firmly upon

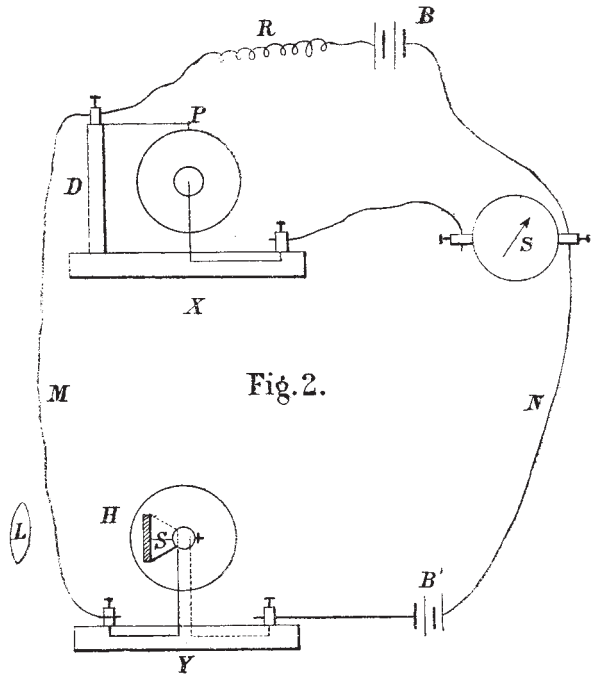

Fig. 2.

the sensitised paper and the selenium exposed to a strong light, the resistance R was varied until the galvanometer needle came to rest at zero. If the two batteries were similar this would occur when the resistance of R was made about equal to that of the selenium cell in the light. The point now made no mark when drawn over the paper. The selenium cell was then darkened, and the point immediately traced a strong brown line; a feeble light was next thrown upon the selenium, and the intensity of

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